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(54) METHOD OF MANUFACTURING CORROSION-RESISTANT RARE EARTH MAGNET

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a corrosion-resistant high-performance rare earth permanent magnet at a low cost.

SOLUTION: Fine powder of one metal selected out of Al, Mg, Ca, Zn, Si, Mn and alloy thereof and an oxide of one or more elements selected out of Si, Mn, Zn, Mo, Cr, and P are compounded into a composite, the composite is formed into a corrosion-resistant film, and the film is provided on the pretreated surface of a rare earth permanent magnet of R-T-M-B (R is, at least, a rare earth element including Y, T denotes Fe of Fe and Co, and M is at least one element selected out of Ti, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, and Ta, and the contents of the elements are represented as follows: $5 \text{ wt.}\% \leq R \leq 40 \text{ wt.}\%$, $50 \text{ wt.}\% \leq T \leq 90 \text{ wt.}\%$, $0.1 \text{ wt.}\% \leq M \leq 8 \text{ wt.}\%$, and $0.2 \text{ wt.}\% \leq B \leq 80 \text{ wt.}\%$).

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CLAIMS

[Claim(s)]

[Claim 1] R-T-M-B (and it Co(es) the rare earth elements in which R contains Y -- at least -- a kind and T -- Fe or Fe --) M is a kind of element chosen from Ti, Nb, aluminum, V, Mn, Sn, calcium, Mg, Pb, Sb, Zn, Si, Zr, Cr, nickel, Cu, Ga, Mo, W, and Ta at least. The content of each element, respectively $5\text{wt}\% \leq R \leq 40\text{wt}\%$, $50\text{wt}\% \leq T \leq 90\text{wt}\%$, On the front face of the rare earth permanent magnet written at $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$ and $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$ The impalpable powder of at least a kind of metal chosen from aluminum, Mg, calcium, Zn, Si, Mn, and these alloys after pretreating. The manufacture approach of the corrosion-resistant rare earth magnet characterized by giving the corrosion-resistant coat which is chosen from Si, Mn, Zn, Mo, Cr, and P, and which compounds the oxide of the element more than a kind at least, and is formed.

[Claim 2] claim 1 -- setting -- a rare earth permanent magnet -- R-T-M-B (the rare earth elements in which R contains Y -- at least -- a kind --) T is a kind of element for which Fe or Fe, and Co and M are chosen from Ti, Nb, aluminum, V, Mn, Sn, calcium, Mg, Pb, Sb, Zn, Si, Zr, Cr, nickel, Cu, Ga, Mo, W, and Ta at least. The alloy 1 with which the content of each element is written at $5\text{wt}\% \leq R \leq 40\text{wt}\%$, $50\text{wt}\% \leq T \leq 90\text{wt}\%$, $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$, and $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$, respectively, R-Fe-Co-M-B (R and M -- the above -- being the same -- the content of each element -- $30\text{wt}\% \leq R \leq 90\text{wt}\%$ --) The manufacture approach of the corrosion-resistant rare earth magnet which mixes the alloy 2 written at $0\text{wt}\% \leq \text{Fe} \leq 50\text{wt}\%$, $5\text{wt}\% \leq \text{Co} \leq 70\text{wt}\%$, $0\text{wt}\% \leq M \leq 8\text{wt}\%$, and $0\text{wt}\% \leq B \leq 2\text{wt}\%$, and is manufactured.

[Claim 3] The manufacture approach of the corrosion-resistant rare earth magnet according to claim 1 or 2 which gave the above-mentioned corrosion-resistant coat after performing processing chosen from acid cleaning, alkali treatment, and blasting processing by considering the front face of the above-mentioned permanent magnet as pretreatment.

[Claim 4] The manufacture approach of a corrosion-resistant rare earth magnet according to claim 1, 2, or 3 that the average thickness of a corrosion-resistant coat is 1-40 micrometers.

[Claim 5] The manufacture approach of claim 1 0.01-5 micrometers and whose aspect ratio (an average major axis / average thickness) a configuration is two or more in an average major axis at flake-like impalpable powder for the metal powder which constitutes a corrosion-resistant coat and whose content rate of the flake-like impalpable powder in a coat is more than 70wt% by 0.1-15 micrometers and average thickness thru/or the corrosion-resistant rare earth magnet of four given in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a corrosion-resistant rare earth magnet of having high corrosion resistance.

[0002]

[Description of the Prior Art] The rare earth permanent magnet is used abundantly in broad fields, such as various electric products and a peripheral device of a computer, for the outstanding magnetic properties, and are the important electrical and electric equipment and an electronic ingredient. Since Nd which is a main element existing in abundance from Sm compared with a Sm-Co system permanent magnet, and Co are not used for a Nd-Fe-B system permanent magnet so much, its material cost is especially cheap, and it is the extremely excellent permanent magnet with which magnetic properties also easily endure a Sm-Co system permanent magnet. For this reason, increasingly, the amount of the Nd-Fe-B system permanent magnet used increases, and an application is also spreading in recent years.

[0003] Although development research for the improvement in magnetic properties has been energetically performed since invention of a Nd-Fe-B system permanent magnet, there are two so-called alloying methods which mix and sinter the alloy powder with which two kinds of the presentations as one differ, and manufacture a high performance Nd magnet. The method of manufacturing the high performance Nd magnet which maintained a high residual magnetic flux density, high coercive force, and the balance that has a high energy product further is proposed by determining the presentation of two kinds of alloys in consideration of the class of magnetic-substance configuration phase, a property, etc., and combining these with patent No. 2853838, patent No. 2853839, JP,5-21218,A, JP,5-21219,A, JP,5-74618,A, and JP,5-182814,A.

[0004] However, since a Nd-Fe-B system permanent magnet contains rare earth elements and iron as a principal component, it has the fault of oxidizing easily in the inside of a short time in the air which wore humidity. For this reason, when it includes in a magnetic circuit, the output of a magnetic circuit declines by these oxidation, or there is a problem with which rust pollutes the device circumference. Since the Nd-Fe-B system permanent magnet created with two alloying methods proposed in an aforementioned patent official report and an aforementioned open patent official report has the presentation containing Co, although corrosion resistance is improving to some extent, it is still inadequate depending on an application.

[0005] Although a Nd-Fe-B system permanent magnet is beginning to be used for motors, such as a motor for automobiles, and a motor for elevators, especially recently, these are obliged to use in a hot and humid environment. Moreover, it must also assume being put to the moisture containing salinity, and it is required that higher corrosion resistance should be realized by low cost. Furthermore, in the production process, although these motors are short time, a magnet may be heated by 300 degrees C or more, and in such a case, they also combine thermal resistance and are required.

[0006] In order to improve the corrosion resistance of a Nd-Fe-B system permanent magnet, in many cases, various surface treatment, such as resin paint, aluminum ion plating, and nickel plating, is performed, but with the technique of a present stage, it is difficult to deal with the above severe conditions by such surface treatment. For example, resin paint does not have thermal resistance, when corrosion resistance runs short. Since a pinhole exists in nickel plating slightly, rust is generated in the moisture containing salinity. although the ion plating of thermal resistance and corrosion resistance is in general good, it is difficult to need large-scale equipment and to realize low cost -- etc. -- there is a problem.

[0007] After this invention was made in order to offer the rare earth permanent magnet which is highly efficient and is equal to use by the above severe conditions in view of the above-mentioned situation, and it pretreats on the front face of a high performance rare earth permanent magnet, it aims at offering the manufacture approach of the corrosion-resistant high performance rare earth magnet which gave the coat which has corrosion resistance and thermal resistance with sufficient adhesion.

[0008]

[The means for solving a technical problem and the gestalt of implementation of invention] The result of having examined wholeheartedly the Nd-Fe-B system permanent magnet which is highly efficient as for this invention person, and has corrosion resistance, R-T-M-B (and it Co(es) the rare earth elements in which R contains Y -- at least -- a kind and T -- Fe or Fe --) M is a kind of element chosen from Ti, Nb, aluminum, V, Mn, Sn, calcium, Mg, Pb, Sb, Zn, Si, Zr, Cr, nickel, Cu, Ga, Mo, W, and Ta at least. The alloy with which the content of each element is written at $5\text{wt}\% \leq R \leq 40\text{wt}\%$, $50\text{wt}\% \leq T \leq 90\text{wt}\%$, $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$, and $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$, respectively, especially this alloy 1, R-Fe-Co-M-B (R and M -- the above -- the same -- the content of each element -- $30\text{wt}\% \leq R \leq 90\text{wt}\%$ --) $0\text{wt}\% \leq \text{Fe} \leq 50\text{wt}\%$, $5\text{wt}\% \leq \text{Co} \leq 70\text{wt}\%$, $0\text{wt}\% \leq M \leq 8\text{wt}\%$, Mix and the alloy 2 written at $0\text{wt}\% \leq B \leq 2\text{wt}\%$ on the front face of the rare earth permanent magnet manufactured The impalpable powder of at least a kind of metal chosen from aluminum, Mg, calcium, Zn, Si, Mn, and these alloys after pretreating preferably, By giving the coat which is chosen from Si, Mn, Zn, Mo, Cr, and P and which compounds the oxide of the element more than a kind at least, and is formed with sufficient adhesion, the knowledge of the ability to offer the rare earth magnet excellent in corrosion resistance and thermal resistance was carried out, terms and conditions were established, and this invention was completed.

[0009] namely, this invention -- (1) R-T-M-B (the rare earth elements in which R contains Y -- at least -- a kind --) T is a kind of element for which Fe or Fe, and Co and M are chosen from Ti, Nb, aluminum, V, Mn, Sn, calcium, Mg, Pb, Sb, Zn, Si, Zr, Cr, nickel, Cu, Ga, Mo, W, and Ta at least. The content of each element, respectively $5\text{wt}\% \leq R \leq 40\text{wt}\%$, $50\text{wt}\% \leq T \leq 90\text{wt}\%$, On the front face of the rare earth permanent magnet written at $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$ and $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$ At least a kind of metal impalpable powder chosen from aluminum, Mg, calcium, Zn, Si, Mn, and these alloys after pretreating, Si -- Mn -- Zn -- Mo -- Cr -- P -- from -- choosing -- having -- at least -- a kind -- more than -- an element -- an oxide -- compounding -- forming -- having -- corrosion resistance -- a coat -- having given -- things -- the description -- ** -- carrying out -- corrosion resistance -- a rare earth magnet --

manufacture -- an approach -- and -- (two --) -- the above -- (one --) -- manufacture -- an approach -- setting -- a rare earth permanent magnet -- R-T-M-B (the rare earth elements in which R contains Y -- at least -- a kind --) T is a kind of element for which Fe or Fe, and Co and M are chosen from Ti, Nb, aluminum, V, Mn, Sn, calcium, Mg, Pb, Sb, Zn, Si, Zr, Cr, nickel, Cu, Ga, Mo, W, and Ta at least. The alloy 1 with which the content of each element is written at $5\text{wt}\% \leq R \leq 40\text{wt}\%$, $50\text{wt}\% \leq T \leq 90\text{wt}\%$, $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$, and $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$, respectively, R-Fe-Co-M-B (R and M -- the above -- being the same -- the content of each element -- $30\text{wt}\% \leq R \leq 90\text{wt}\%$ --) The alloy 2 written at $0\text{wt}\% \leq \text{Fe} \leq 50\text{wt}\%$, $5\text{wt}\% \leq \text{Co} \leq 70\text{wt}\%$, $0\text{wt}\% \leq M \leq 8\text{wt}\%$, and $0\text{wt}\% \leq B \leq 2\text{wt}\%$ is mixed, and the manufacture approach of the corrosion-resistant rare earth magnet manufactured is offered.

[0010] Hereafter, this invention is explained to a detail. In manufacturing the Nd-Fe-B system permanent magnet used for this invention R-T-M-B (and it Co(es) the rare earth elements in which R contains Y -- at least -- a kind and T -- Fe or Fe --) M is a kind of element chosen from Ti, Nb, aluminum, V, Mn, Sn, calcium, Mg, Pb, Sb, Zn, Si, Zr, Cr, nickel, Cu, Ga, Mo, W, and Ta at least. The content of each element, respectively $5\text{wt}\% \leq R \leq 40\text{wt}\%$, $50\text{wt}\% \leq T \leq 90\text{wt}\%$, The rare earth permanent magnet written at $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$ and $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$, especially -- R-T-M-B (and it Co(es) the rare earth elements in which R contains Y -- at least -- a kind and T -- Fe or Fe --) M is a kind of element chosen from Ti, Nb, aluminum, V, Mn, Sn, calcium, Mg, Pb, Sb, Zn, Si, Zr, Cr, nickel, Cu, Ga, Mo, W, and Ta at least. The alloy 1 with which the content of each element is written at $5\text{wt}\% \leq R \leq 40\text{wt}\%$, $50\text{wt}\% \leq T \leq 90\text{wt}\%$, $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$, and $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$, respectively, R-Fe-Co-M-B (R and M -- the above -- being the same -- the content of each element -- $30\text{wt}\% \leq R \leq 90\text{wt}\%$ --) The alloy 2 written at $0\text{wt}\% \leq \text{Fe} \leq 50\text{wt}\%$, $5\text{wt}\% \leq \text{Co} \leq 70\text{wt}\%$, $0\text{wt}\% \leq M \leq 8\text{wt}\%$, and $0\text{wt}\% \leq B \leq 2\text{wt}\%$ is mixed, and the rare earth permanent magnet manufactured with two so-called alloying methods is prepared.

[0011] Here, an alloy 1 uses an R₂Fe₁₄B compound phase (for R, the rare earth elements containing Y are kinds at least) as a principal component, and what mainly becomes the main phase of Nd magnet is [after sintering] desirable. an alloy 1 -- a raw material metal -- a vacuum or inert gas -- it dissolves and creates in Ar ambient atmosphere preferably. Although a raw material metal uses pure rare earth elements, a rare earth alloy, pure iron, ferroborons, these alloys, etc., in industrial production, C, N, O, H, P, S, etc. make it typically various unescapable impurities and the thing contained. Although alphaFe, R rich phase, B rich phase, etc. may remain other than R₂Fe₁₄B phase, since the direction with many R₂Fe₁₄B phases in an alloy 1 is desirable, the obtained alloy performs solution treatment if needed in creation of a high performance Nd magnet. What is necessary is just to heat-treat the conditions at that time at the temperature of 700-1,200 degrees C under a vacuum or Ar ambient atmosphere for 1 hour or more.

[0012] on the other hand -- an alloy 2 -- R-Fe-Co-M-B (the content of each element -- $30\text{wt}\% \leq R \leq 90\text{wt}\%$ --) $0\text{wt}\% \leq \text{Fe} \leq 50\text{wt}\%$, $5\text{wt}\% \leq \text{Co} \leq 70\text{wt}\%$, $0\text{wt}\% \leq M \leq 8\text{wt}\%$, it being written at $0\text{wt}\% \leq B \leq 2\text{wt}\%$ and making Pr, Dy, or Tb indispensable as R further -- desirable -- an alloy 1 -- the same -- a raw material metal -- a vacuum or inert gas -- it dissolves and creates in Ar ambient atmosphere preferably. a raw material metal -- pure rare earth elements, a rare earth alloy, pure iron, ferroboron, and pure cobalt -- although these alloys etc. are used further, in industrial production, C, N, O, H, P, S, etc. are typically taken as various unescapable impurities and the thing contained. Into the alloy obtained in this presentation, R₂T₁₄B phase (transition-metals element with which T₁ makes Fe and Co a subject), A RT₂₄L phase, RT₂₃ phase, RT₂₂ phase, R₂T₂₇B phase, RT₂₅ phase (one sort or two sorts, and L are B, or B and M among the transition-metals element with which T₂ makes Fe and Co a subject, these transition metals, and M), etc. appear in R rich phase and a list. All, for below the melting point of R₂Fe₁₄B phase, an alloy 2 has moderate viscosity in sintering temperature, and the melting point of these phases serves as a liquid phase component which does not disturb grained orientation but cleans a grain boundary. Although an alloy 2 is the presentation containing many rare earth elements which are easy to oxidize, oxidation is controlled by using Co.

[0013] After grinding separately the alloy 1 and alloy 2 which were described above, respectively, those powder is mixed to a predetermined ratio. Although grinding is generally performed on coarse grinding, pulverizing, and a phase target, mixing may be performed in any phase. However, as for two alloy powder, it is desirable that homogeneity is mixed with the almost same mean particle diameter, and the range of mean particle diameter of 0.5-20 micrometers is good. In less than 0.5 micrometers, there is a possibility that magnetic properties may fall that it is easy to oxidize. Moreover, when it exceeds 20 micrometers, there is a possibility that a degree of sintering may worsen.

[0014] 1 - $30\text{wt}\%$ of the mixing ratio of the powder of an alloy 1 and an alloy 2 has [an alloy 1] a desirable alloy 2 70 - 99wt%. If an alloy 2 is less than [1wt%], there are too few liquid phase components, sintered density does not go up, and sufficient coercive force may not be acquired. When an alloy 2 exceeds $30\text{wt}\%$, there is a possibility that the rate of the nonmagnetic phase after sintering may be too large, and a residual magnetic flux density may become small.

[0015] The mixed mixed fines are fabricated by the predetermined configuration and sinter by continuing with the molding press in a magnetic field. It is desirable to perform sintering 30 minutes or more under a vacuum or Ar ambient atmosphere in a 900-1,200-degree C temperature requirement, and to carry out aging heat treatment 30 minutes or more at the low temperature below sintering temperature further after sintering.

[0016] In the Nd-Fe-B system permanent magnet in this invention, what has the concentration segregation of Pr, Dy, and/or Tb in a grain boundary periphery is good. This has the effectiveness that this raises magnetic coercive force more, although Pr, Tb, and Dy which are contained in the alloy 2 of a liquid phase component are because it is not spread completely but after sintering exists near the grain boundary in the main phase. For this reason, even if it is the same presentation, a magnet with higher magnetic properties can be manufactured.

[0017] As for the Nd-Fe-B system permanent magnet in this invention, it is desirable that magnetic properties are three or more 239 kJ/m in more than 1.1T and coercive force iH_c at a residual magnetic flux density B_r, and in industrial production, although C, N, O, H, P, S, etc. are contained typically, as for the total, it is still more desirable at 796 or more kA/m and maximum energy product (BH) max an unescapable impurity element and that it is less than [2wt%]. When 2wt(s)% is exceeded, there is a possibility that the nonmagnetic component in a permanent magnet may increase and a residual magnetic flux density may become small. Moreover, there is a possibility that rare earth elements may be consumed by these impurities, and may become poor sintering, and coercive force may become low. As total of an impurity is low, a residual magnetic flux density and its coercive force become high and are more desirable.

[0018] The sintered compact consistency of the Nd-Fe-B system permanent magnet in this invention has desirable cc in 7.2g /or more. By cc, coercive force may not fully be acquired in less than 7.2g /. Moreover, as for anti-****, 500 or more are desirable at 150 or more MPas and Vickers hardness number. There is a possibility that anti-**** may be damaged when less than 500 permanent magnet is actually used by a motor etc. by less than 150 MPas and Vickers hardness number.

[0019] In this invention, the corrosion-resistant coat which compounds the impalpable powder of at least a kind of metal chosen from aluminum, Mg, calcium, Zn, Si, Mn, and these alloys and the oxide of at least a kind of element chosen from Si, Mn, Zn, Mo, Cr, and P, and is formed in the front face of the above-mentioned rare earth permanent magnet is formed.

[0020] As the above-mentioned metal impalpable powder, it is desirable that it is flake-like impalpable powder here, an average major

axis is [0.1-15 micrometers and average thickness] 0.01-5 micrometers, and two or more things have [the configuration] a desirable aspect ratio (an average major axis / average thickness). More preferably, an average major axis is 1-10 micrometers, and average thickness is 0.1-0.3 micrometers, and aspect ratios (an average major axis / average thickness) are ten or more things. An average major axis does not carry out a laminating in parallel [flake-like impalpable powder] with a base in less than 0.1 micrometers, but there is a possibility that the adhesion force may be insufficient. If an average major axis exceeds 15 micrometers, at the time of heating printing, a flake may be lifted with the moisture which evaporated, and a laminating may not be carried out in parallel with a base, but, as a result, it may become the bad coat of adhesion. Moreover, an average major axis has desirable 15 micrometers or less on the dimensional accuracy of a coat. A possibility that distribution of the flake in the inside of said distributed water solution will worsen, average thickness will become easy to sediment if a flake front face oxidizes in the manufacture phase of a flake, the film becomes weak, a less than 0.01-micrometer thing serves as the inclination for corrosion resistance to tend to get worse and average thickness exceeds 5 micrometers, processing liquid may become unstable, and corrosion resistance may worsen as a result is. When an aspect ratio is less than two, there is a possibility that a flake may become poor adhesion that it is hard to carry out a laminating in parallel with a base. Although there is no upper limit of an aspect ratio, a not much large thing becomes high in cost, and is usually 50 or less.

[0021] In the coat formed by this invention, the content of the above-mentioned metal impalpable powder, especially flake-like impalpable powder is more than 70wt%, and is more than 75wt% more preferably. Since there is [to be fully unable to cover a magnet base] too little impalpable powder less than [70wt%], there is a possibility that corrosion resistance may fall. Moreover, it is good less than [30wt%] and for the oxide of at least a kind of element chosen from Si, Mn, Zn, Mo, Cr, and P to add less than [25wt%] (for 0 not to be included) more preferably.

[0022] In this invention, although the approach apply the above-mentioned permanent magnet to the distributed water solution of the above-mentioned metal impalpable powder and the above-mentioned oxide, and it applies immersion or this water solution to a permanent magnet can adopt the approach of forming the above-mentioned corrosion-resistant coat, it is desirable to pretreat on the surface of a magnet first in this case. What is necessary is just to perform at least one kind of processing which is chosen from acid treatment, alkali treatment, and blasting processing, and is chosen from (1) acid cleaning, rinsing, ultrasonic cleaning, (2) alkali cleaning, rinsing, (3) shot blasting, etc. as pretreatment. as a penetrant remover used by (1), it is chosen from a nitric acid, a hydrochloric acid, an acetic acid, a citric acid, formic acid, a sulfuric acid, a hydrofluoric acid, permanganic acid, oxalic acid, hydroxyacetic acid, and phosphoric acid -- at least -- more than a kind -- the sum total -- 1 - 20wt% -- using the included water solution, this is made into the temperature of 80 degrees C or less beyond ordinary temperature, and a rare earth magnet is immersed. By performing acid cleaning, a surface oxide film can be removed and it is effective in raising the adhesion force of said coat. The alkali-cleaning liquid which can be used by (2) is water solutions which contain more than a kind 5 or more g/L 200 or less g/L in total at least, such as a sodium hydroxide, a sodium carbonate, an orthochromatic sodium silicate, a meta-sodium silicate, trisodium phosphate, a sodium cyanide, and a chelating agent, makes this the temperature of 90 degrees C or less beyond ordinary temperature, and should just be immersed in a rare earth magnet. Alkali cleaning is effective in removing the dirt of fats and oils adhering to a magnet front face, and raises the adhesion force between said coats and magnets. What is necessary is to be able to use the usual ceramics, glass, plastics, etc. as abrasive of (3), and just to process by the discharge pressure 2 - 3 kgf/cm². Shot blasting can remove the oxide film on the front face of a magnet by dry type, and is effective in raising adhesion too.

[0023] Following pretreatment, a permanent magnet is applied to the distributed water solution of metal impalpable powder and the above-mentioned oxide, and immersion or this water solution is applied to a permanent magnet. After immersion or spreading, although heat-treatment is performed, as for temperature, it is desirable to maintain 30 minutes or more at 300 degrees C or more less than 350 degrees C. Less than 300 degrees C of membrane formation are insufficient, and there is a possibility that the adhesion force and corrosion resistance may worsen. Moreover, if it is made 350 degrees C or more, the magnet of a substrate receives a damage and can cause magnetic-properties degradation.

[0024] If in charge of formation of the coat in this invention, two coats and heat-treatment may be performed repeatedly. The coat in this invention serves as the structure where metal impalpable powder, especially flake-like impalpable powder were combined with the indeterminate form oxide. Although the reason this shows high corrosion resistance is not certain, when impalpable powder is a flake-like, in general in parallel with a base, a magnet is covered well and this is considered [a set and] with a shielding effect. Moreover, when a metal or an alloy with **** potential is used from a permanent magnet as flake-like impalpable powder, these oxidize previously and are considered that there is effectiveness which controls oxidation of the magnet of a substrate. Moreover, since this coat is an inorganic substance, it also has the description that thermal resistance is high compared with an organic coat.

[0025] Thus, as for the average thickness of the coat of obtained this invention, it is desirable that it is in the range of 1-40 micrometers. In less than 1 micrometer, if corrosion resistance may be insufficient and it exceeds 40 micrometers, the case where it lifting-comes to be easy of an adhesion force fall and interlaminar peeling will arise. Furthermore, since the volume of the R-Fe-B system permanent magnet which can be used will become small even if an appearance configuration is the same if a coat is thickened, a magnet use top is not desirable, either.

[0026]

[Example] Although an example is shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0027] First, the rare earth permanent magnet was manufactured by the following approach. the RF dissolution of Ar ambient atmosphere -- a weight ratio -- 28Nd-69.8Fe-1Co-1B-0.2aluminum -- the ingot of a presentation was produced and solution treatment was carried out at 1,070 degrees C under Ar ambient atmosphere for 20 hours. Let this be an alloy 1. next -- the same -- a weight ratio -- 47Nd-13Dy-18.3Fe-20Co-0.5B-1Cu-0.2aluminum -- the ingot of a presentation was produced by the RF dissolution of Ar ambient atmosphere. Let this be an alloy 2. Coarse grinding of the ingot of an alloy 1 and an alloy 2 was carried out with the jaw crusher under nitrogen-gas-atmosphere mind according to, respectively, and it mixed continuously for 30 minutes with V blender which carried out weighing capacity of the coarse powder 7wt% of the alloy 2 to coarse powder 93wt% of the alloy 1, and carried out the nitrogen purge to it. This mixed coarse powder was further pulverized with the jet mill under nitrogen gas, and the impalpable powder whose mean particle diameter is 3 micrometers was obtained. It was filled up with this impalpable powder in the metal mold impressed to 15kOe field, and it carried out press forming by the pressure of 2 cm 1.0t /. This Plastic solid was sintered at 1,070 degrees C under Ar ambient atmosphere for 2 hours, performed aging treatment at 530 more degrees C for 1 hour, and used it as the permanent magnet. Ultrasonic rinsing was performed and this was made into the magnet test piece, after starting the piece of a magnet of 21mm x thickness dimension of 10mm of diameters from the obtained permanent magnet and performing barrel finishing processing.

[0028] When the magnetic properties of this magnet were measured with BH marker, for the residual magnetic flux density Br, 14.4T and coercive force iHc were [1,110 kA/m and a maximum energy product] 398 kJ/m³. When the element distribution of Dy in this magnet was investigated in EPMA, distribution of Dy existed near the grain boundary of the main phase mostly, and the center of the

main phase had little distribution of Dy.

[0029] The various impurity elements contained in this magnet, and when weight, such as C, N, O, H, P, and S, was measured using inert gas fusion infrared absorption spectrometry, inert gas heat-of-fusion conductometry, combustion infrared absorption spectrometry, etc., that total was specifically 0.5wt(s)%. The sintered compact consistency was 7.55g/cc. It was 240MPa when anti-**** was measured by the three-point bending method according to JIS-R -1601. It was 600 when Vickers hardness number was measured by the 9.807-N load using the Vickers hardness meter.

[0030] Next, the distributed water solution with which chromic anhydride 4wt% was contained was prepared flake-like aluminium-powder 2wt% as processing liquid for coat formation flake-like zinc powder 20wt% (both 0.2 micrometers in the average major axis of 3 micrometers, average thickness). After performing pretreatment shown in Table 1 on said magnet test piece front face and immersing said test piece in this distributed water solution, **** was removed by the spin coater which adjusted the rotational frequency so that it might become 10-micrometer thickness, and it heated at 330 degrees C at the hot-air-drying furnace for 30 minutes, and said coat was formed. The detail of pretreatment is as follows.

Acid-cleaning presentation: 10% (v/v) of nitric acids, 5% (v/v) of sulfuric acids

50 degrees C -- 30-minute immersion alkali-cleaning presentation: -- sodium-hydroxide 10 g/L, meta-sodium-silicate 3g/L, trisodium phosphate 10 g/L, sodium-carbonate 8 g/L, and surface-active-agent 2 g/L40 degree C -- for 2 minutes -- the aluminum oxide of immersion shot-blasting #220 -- using -- discharge-pressure 2 kgf/cm² -- processing [0031] Subsequently, the squares adhesion test was performed by the following approach to the obtained coat.

It applies to squares adhesion test (1) JIS-K-5400 cross cut adhesion test. After putting in an incised wound in a grid pattern so that 100 1mm masses may be made with a cutter knife at a coat, a cellophane tape is pushed strongly, it lengthens at the include angle of 45 degrees strongly, and removes, and the number of the squares which remained estimates adhesion. (2) 120 degrees C, two atmospheric pressures, and the pressure cooker trial of 200 hours were performed to the magnet in which the coat was formed, and the squares adhesion test was performed to the magnet after this trial. After they put in the incised wound in a grid pattern according to JIS-K-5400 cross cut adhesion test so that 100 1mm masses might be made with a cutter knife at a coat, the contents of a trial pushed the cellophane tape strongly, they were strongly lengthened at the include angle of 45 degrees, removed, and evaluated adhesion by the number of the squares which remained. It combines with the example 1 of a comparison which did not pretreat, and a result is shown in Table 1. By pretreating shows that the adhesion force is improving further.

[0032]

[Table 1]

	前処理	(1)基盤目密着性試験	(2)ブレッシャーグロッター試験後 基盤目密着性試験
実施例 1	酸洗浄+水洗+超音波洗浄	100/100	100/100
実施例 2	アルカリ洗浄+水洗	100/100	100/100
実施例 3	ショットブラスト	100/100	100/100
比較例 1	なし	100/100	80/100

[0033]

[Effect of the Invention] The impalpable powder of at least a kind of metal chosen from aluminum, Mg, calcium, Zn, Si, Mn, and these alloys after pretreating preferably on the front face of a high performance rare earth permanent magnet according to this invention, By giving the coat which is chosen from Si, Mn, Zn, Mo, Cr, and P and which compounds the oxide of the element more than a kind at least, and is formed with sufficient adhesion, a corrosion-resistant high performance rare earth permanent magnet can be offered cheaply, and the utility value is very high on industry.

[Translation done.]

7/7

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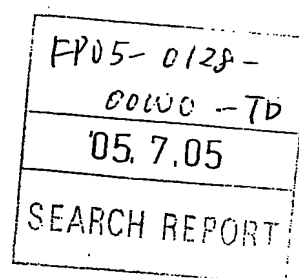
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(54) 【発明の名称】 耐食性希土類磁石の製造方法

(57) 【要約】 (修正有)

【解決手段】 R-T-M-B (RはYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ $5\text{wt}\% \leq R \leq 40\text{wt}\%$ 、 $50\text{wt}\% \leq T \leq 90\text{wt}\%$ 、 $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$ 、 $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$) で表記される希土類永久磁石の表面に、前処理を施した後、Al, Mg, Ca, Zn, Si, Mn及びこれらの合金の中から選ばれる金属の微粉末と、Si, Mn, Zn, Mo, Cr, Pから選ばれる元素の酸化物を複合して形成される耐食性皮膜を付与する。

【効果】 耐食性高性能希土類永久磁石を安価に提供することができる。



【特許請求の範囲】

【請求項1】 R-T-M-B (RはYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ $5\text{wt}\% \leq R \leq 40\text{wt}\%$ 、 $50\text{wt}\% \leq T \leq 90\text{wt}\%$ 、 $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$ 、 $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$) で表記される希土類永久磁石の表面に、前処理を施した後、Al, Mg, Ca, Zn, Si, Mn及びこれらの合金の中から選ばれる少なくとも一種の金属の微粉末と、Si, Mn, Zn, Mo, Cr, Pから選ばれる少なくとも一種以上の元素の酸化物を複合して形成される耐食性皮膜を付与したことを特徴とする耐食性希土類磁石の製造方法。

【請求項2】 請求項1において、希土類永久磁石が、R-T-M-B (RはYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ $5\text{wt}\% \leq R \leq 40\text{wt}\%$ 、 $50\text{wt}\% \leq T \leq 90\text{wt}\%$ 、 $0.1\text{wt}\% \leq M \leq 8\text{wt}\%$ 、 $0.2\text{wt}\% \leq B \leq 8\text{wt}\%$) で表記される合金1と、R-Fe-Co-M-B (R及びMは上記と同じであって、各元素の含有量が $30\text{wt}\% \leq R \leq 90\text{wt}\%$ 、 $0\text{wt}\% \leq \text{Fe} \leq 50\text{wt}\%$ 、 $5\text{wt}\% \leq \text{Co} \leq 70\text{wt}\%$ 、 $0\text{wt}\% \leq M \leq 8\text{wt}\%$ 、 $0\text{wt}\% \leq B \leq 2\text{wt}\%$) で表記される合金2を混合し、製造されたものである耐食性希土類磁石の製造方法。

【請求項3】 上記永久磁石の表面を前処理として、酸洗浄、アルカリ処理、プラスト処理から選択される処理を施した後、上記耐食性皮膜を付与するようにした請求項1又は2記載の耐食性希土類磁石の製造方法。

【請求項4】 耐食性皮膜の平均厚みが $1 \sim 40\mu\text{m}$ である請求項1、2又は3記載の耐食性希土類磁石の製造方法。

【請求項5】 耐食性皮膜を構成する金属粉末がフレーク状微粉末で、形状が平均長径で $0.1 \sim 15\mu\text{m}$ 、平均厚さで $0.01 \sim 5\mu\text{m}$ 、アスペクト比(平均長径/平均厚さ)が2以上であるものであって、皮膜内におけるフレーク状微粉末の含有割合が $70\text{wt}\%$ 以上である請求項1乃至4のいずれか1項記載の耐食性希土類磁石の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、高耐食性を有する耐食性希土類磁石の製造方法に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】 希土類永久磁石は、その優れた磁気特性のため各種電気製品やコンピュータの周辺機器等、幅広い分野で多用されており、重要な電気、電子材料である。特にNd-Fe-B系永久磁石は、Sm-Co系永久磁石に比べて主要元素であるNdがSmより豊富に存在すること、Coを多量に使用しないことから原材料費が安価であり、磁気特性もSm-Co系永久磁石をはるかにしのぐ極めて優れた永久磁石である。このため、近年ますますNd-Fe-B系永久磁石の使用量は増大し、用途も広がっている。

【0003】 磁気特性向上のための開発研究はNd-Fe-B系永久磁石の発明以来精力的に行われているが、その1つとして、2種類の組成の異なる合金粉末を混合、焼結して高性能Nd磁石を製造する、いわゆる2合金法がある。特許第2853838号、特許第2853839号、特開平5-21218号、特開平5-21219号、特開平5-74618号、特開平5-182814号公報には、磁性体構成相の種類、特性等を考慮して2種類の合金の組成を決定し、これらを組み合わせることにより、高残留磁束密度と高保磁力、更に高エネルギー積を有するバランスのとれた高性能Nd磁石を製造する方法が提案されている。

【0004】 しかし、Nd-Fe-B系永久磁石は、主成分として希土類元素及び鉄を含有するため、湿度をおびた空气中で短時間の内に容易に酸化するという欠点を持っている。このため、磁気回路に組み込んだ場合には、これらの酸化により磁気回路の出力が低下したり、錆が機器周辺を汚染する問題がある。前記の特許公報及び公開特許公報で提案されている2合金法で作成されたNd-Fe-B系永久磁石は、Coを含んだ組成を有するため、耐食性はある程度向上しているが、それでも用途によっては不十分である。

【0005】 特に、最近は自動車用モータやエレベータ用モータなどのモータ類にもNd-Fe-B系永久磁石が使われはじめているが、これらは高温かつ湿潤な環境での使用を余儀なくされる。また、塩分を含んだ湿気に曝されることも想定しなくてはならず、より高い耐食性を低コストで実現することが要求されている。更に、これらのモータ類は、その製造工程において、短時間ではあるが磁石が 300°C 以上に加熱されることがあり、このような場合には耐熱性も併せて要求される。

【0006】 Nd-Fe-B系永久磁石の耐食性を改善するため、多くの場合、樹脂塗装、Alイオンプレーティング、Niメッキ等の各種表面処理が施されるが、上記のような厳しい条件にこれらの表面処理で対応することは現段階の技術では難しい。例えば、樹脂塗装は耐食性が不足する上、耐熱性がない。Niメッキにはピンホールがわずかながら存在するため、塩分を含んだ湿気中では錆が発生する。イオンプレーティングは耐熱性、耐

食性は概ね良好であるが、大掛かりな装置を必要とし、低コストを実現するのは困難である、などの問題がある。

【0007】本発明は、上記事情に鑑み、高性能で、かつ上記のような過酷な条件での使用に耐える希土類永久磁石を提供するためになされたもので、高性能希土類永久磁石の表面に、前処理を施した後、耐食性、耐熱性を有する皮膜を密着性よく付与した、耐食性高性能希土類磁石の製造方法を提供することを目的とする。

【0008】

【課題を解決するための手段及び発明の実施の形態】本発明者は、高性能でかつ耐食性を有するNd-Fe-B系永久磁石について鋭意検討した結果、R-T-M-B (RはYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi、Nb、Al、V、Mn、Sn、Ca、Mg、Pb、Sb、Zn、Si、Zr、Cr、Ni、Cu、Ga、Mo、W、Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ5wt% \leq R \leq 40wt%、50wt% \leq T \leq 90wt%、0.1wt% \leq M \leq 8wt%、0.2wt% \leq B \leq 8wt%)で表記される合金、特に該合金1と、R-Fe-Co-M-B (R及びMは上記と同様であり、各元素の含有量が30wt% \leq R \leq 90wt%、0wt% \leq Fe \leq 50wt%、5wt% \leq Co \leq 70wt%、0wt% \leq M \leq 8wt%、0wt% \leq B \leq 2wt%)で表記される合金2とを混合し、製造される希土類永久磁石の表面に、好ましくは前処理を施した後、Al、Mg、Ca、Zn、Si、Mn及びこれらの合金の中から選ばれる少なくとも一種の金属の微粉末と、Si、Mn、Zn、Mo、Cr、Pから選ばれる少なくとも一種以上の元素の酸化物を複合して形成される皮膜を密着性よく付与することにより、耐食性、耐熱性に優れた希土類磁石を提供できることを知見し、諸条件を確立して本発明を完成させた。

【0009】即ち、本発明は、(1) R-T-M-B

(RはYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi、Nb、Al、V、Mn、Sn、Ca、Mg、Pb、Sb、Zn、Si、Zr、Cr、Ni、Cu、Ga、Mo、W、Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ5wt% \leq R \leq 40wt%、50wt% \leq T \leq 90wt%、0.1wt% \leq M \leq 8wt%、0.2wt% \leq B \leq 8wt%)で表記される希土類永久磁石の表面に、前処理を施した後、Al、Mg、Ca、Zn、Si、Mn及びこれらの合金の中から選ばれる少なくとも一種の金属微粉末と、Si、Mn、Zn、Mo、Cr、Pから選ばれる少なくとも一種以上の元素の酸化物を複合して形成される耐食性皮膜を付与したことを特徴とする耐食性希土類磁石の製造方法、及び、(2)上記(1)の製造方法において、希土類永久磁石が、R-T-M-B (R

はYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi、Nb、Al、V、Mn、Sn、Ca、Mg、Pb、Sb、Zn、Si、Zr、Cr、Ni、Cu、Ga、Mo、W、Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ5wt% \leq R \leq 40wt%、50wt% \leq T \leq 90wt%、0.1wt% \leq M \leq 8wt%、0.2wt% \leq B \leq 8wt%)で表記される合金1と、R-Fe-Co-M-B (R及びMは上記と同じであって、各元素の含有量が30wt% \leq R \leq 90wt%、0wt% \leq Fe \leq 50wt%、5wt% \leq Co \leq 70wt%、0wt% \leq M \leq 8wt%、0wt% \leq B \leq 2wt%)で表記される合金2とを混合し、製造されたものである耐食性希土類磁石の製造方法を提供する。

【0010】以下、本発明を詳細に説明する。本発明に用いられるNd-Fe-B系永久磁石を製造するにあたっては、R-T-M-B (RはYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi、Nb、Al、V、Mn、Sn、Ca、Mg、Pb、Sb、Zn、Si、Zr、Cr、Ni、Cu、Ga、Mo、W、Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ5wt% \leq R \leq 40wt%、50wt% \leq T \leq 90wt%、0.1wt% \leq M \leq 8wt%、0.2wt% \leq B \leq 8wt%)で表記される希土類永久磁石、特にR-T-M-B (RはYを含む希土類元素の少なくとも一種、TはFe又はFe及びCo、MはTi、Nb、Al、V、Mn、Sn、Ca、Mg、Pb、Sb、Zn、Si、Zr、Cr、Ni、Cu、Ga、Mo、W、Taから選ばれる少なくとも一種の元素であって、各元素の含有量がそれぞれ5wt% \leq R \leq 40wt%、50wt% \leq T \leq 90wt%、0.1wt% \leq M \leq 8wt%、0.2wt% \leq B \leq 8wt%)で表記される合金1と、R-Fe-Co-M-B (R及びMは上記と同じであって、各元素の含有量が30wt% \leq R \leq 90wt%、0wt% \leq Fe \leq 50wt%、5wt% \leq Co \leq 70wt%、0wt% \leq M \leq 8wt%、0wt% \leq B \leq 2wt%)で表記される合金2とを混合し、いわゆる2合金法で製造される希土類永久磁石を用意する。

【0011】ここで、合金1はR₂Fe₁₄B化合物相

(RはYを含む希土類元素の少なくとも一種)を主成分とし、焼結後は主としてNd磁石の主相になるものが好ましい。合金1は原料金属を真空又は不活性ガス、好ましくはAr雰囲気中で溶解して作成する。原料金属は純希土類元素、希土類合金、純鉄、フェロボロン、更にはこれらの合金等を使用するが、工業生産において不可避な各種不純物、代表的にはC、N、O、H、P、S等に含まれるものとする。得られた合金はR₂Fe₁₄B相の他に α Fe、Rリッチ相、Bリッチ相などが残る場合があるが、高性能Nd磁石の作成にあたっては合金1の中

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の $R_2Fe_{14}B$ 相が多い方が望ましいので、必要に応じて溶体化処理を行う。その時の条件は真空又は Ar 雰囲気下、 $700 \sim 1,200^\circ C$ の温度で1時間以上熱処理すればよい。

【0012】一方、合金2は、 $R-Fe-Co-M-B$ （各元素の含有量が $30wt\% \leq R \leq 90wt\%$ 、 $0wt\% \leq Fe \leq 50wt\%$ 、 $5wt\% \leq Co \leq 70wt\%$ 、 $0wt\% \leq M \leq 8wt\%$ 、 $0wt\% \leq B \leq 2wt\%$ ）で表記され、更に R として Pr 、 Dy 又は Tb を必須とすることが好ましく、合金1と同じく原料金属を真空又は不活性ガス、好ましくは Ar 雰囲気中で溶解して作成する。原料金属は純希土類元素、希土類合金、純鉄、フェロボロン、純コバルト、更にはこれらの合金等を使用するが、工業生産において不可避な各種不純物、代表的には C 、 N 、 O 、 H 、 P 、 S 等は含まれるものとする。この組成において得られた合金には、 $R_2T_{14}B$ 相（ T は Fe 、 Co を主体とする遷移金属元素）、 R リッチ相、並びに RT_2L 相、 RT_3 相、 RT_2 相、 R_2T_7B 相、 RT_5 相（ T は Fe 、 Co を主体とする遷移金属元素、同遷移金属及び M のうち1種又は2種、 L は B 又は B と M ）等が出現する。これらの相の融点はいずれも $R_2Fe_{14}B$ 相の融点以下のため、合金2は、焼結温度において適度な粘度を持ち、粒の配向を乱さず粒界をクリーニングする液相成分となる。合金2は酸化し易い希土類元素を多く含む組成であるが、 Co を用いることにより、酸化を抑制している。

【0013】上記で述べた合金1と合金2をそれぞれ別々に粉砕した後、それらの粉末を所定の比に混合する。粉砕は一般に粗粉砕、微粉砕と段階的に行われるが、混合はどの段階で行ってもよい。但し、2つの合金粉末はほぼ同じ平均粒径で均一に混合されることが好ましく、平均粒径は $0.5 \sim 20 \mu m$ の範囲がよい。 $0.5 \mu m$ 未満では酸化され易く磁気特性が低下してしまうおそれがある。また、 $20 \mu m$ を超えると焼結性が悪くなるおそれがある。

【0014】合金1と合金2の粉末の混合比は合金1が $70 \sim 99wt\%$ 、合金2が $1 \sim 30wt\%$ が好ましい。合金2が $1wt\%$ 未満だと液相成分が少なすぎて焼結密度が上がらず、十分な保磁力が得られない場合がある。合金2が $30wt\%$ を超えると焼結後の非磁性相の割合が大きすぎて残留磁束密度が小さくなるおそれがある。

【0015】混合された混合微粉は、磁場中成形プレスによって所定の形状に成形され、続いて焼結を行う。焼結は $900 \sim 1,200^\circ C$ の温度範囲で真空又は Ar 雰囲気下にて30分以上行い、焼結後、更に焼結温度以下の低温で30分以上時効熱処理することが好ましい。

【0016】本発明における $Nd-Fe-B$ 系永久磁石においては、粒界周辺部に Pr 、 Dy 及び／又は Tb の濃度偏析を有するものがよい。これは液相成分の合金2

に含まれる Pr 、 Tb 、 Dy が主相の中に完全に拡散せず、焼結後も粒界近傍に存在するためであるが、このことが磁石の保磁力をより向上させる効果を持っている。このため、同じ組成であってもより高い磁気特性を持つ磁石が製造できる。

【0017】本発明における $Nd-Fe-B$ 系永久磁石は、磁気特性が残留磁束密度 B_r で $1.1T$ 以上、保磁力 iH_c で $796kA/m$ 以上、最大エネルギー積 $(BH)_{max}$ で $239kJ/m^3$ 以上であることが好ましく、更に工業生産において不可避な不純物元素、代表的には C 、 N 、 O 、 H 、 P 、 S 等が含まれるが、その総和は $2wt\%$ 以下であることが望ましい。 $2wt\%$ を超えると永久磁石中の非磁性成分が多くなって残留磁束密度が小さくなるおそれがある。また、希土類元素がこれら不純物に消費されてしまい、焼結不良になり、保磁力が低くなるおそれがある。不純物の総和は低ければ低いほど残留磁束密度、保磁力共に高くなり好ましい。

【0018】本発明における $Nd-Fe-B$ 系永久磁石の焼結体密度は $7.2g/cc$ 以上が望ましい。 $7.2g/cc$ 未満では保磁力が十分に得られない場合がある。また、抗折力は $150MPa$ 以上、ビッカース硬さで 500 以上が望ましい。抗折力が $150MPa$ 未満、ビッカース硬さで 500 未満の永久磁石は、実際にモータなどで使用された時に破損するおそれがある。

【0019】本発明においては、上記希土類永久磁石の表面に、 Al 、 Mg 、 Ca 、 Zn 、 Si 、 Mn 及びこれらの合金から選ばれる少なくとも一種の金属の微粉末と、 Si 、 Mn 、 Zn 、 Mo 、 Cr 、 P から選ばれる少なくとも一種の元素の酸化物とを複合して形成される耐食性皮膜を形成する。

【0020】ここで、上記金属微粉末としては、フレーク状微粉末であることが好ましく、その形状は、平均長径が $0.1 \sim 15 \mu m$ 、平均厚さが $0.01 \sim 5 \mu m$ であって、かつアスペクト比（平均長径／平均厚さ）が2以上のものが好ましい。より好ましくは、平均長径が $1 \sim 10 \mu m$ 、平均厚さが $0.1 \sim 0.3 \mu m$ であって、かつアスペクト比（平均長径／平均厚さ）が10以上のものである。平均長径が $0.1 \mu m$ 未満では、フレーク状微粉末が素地に平行に積層せず、密着力が不足するおそれがある。平均長径が $15 \mu m$ を超えると、加熱焼付けの時、蒸発した水分によりフレークが持ち上げられ、素地に平行に積層せず、その結果密着の悪い皮膜になってしまう場合がある。また、皮膜の寸法精度上、平均長径は $15 \mu m$ 以下が望ましい。平均厚さが $0.01 \mu m$ 未満のものは、フレークの製造段階でフレーク表面が酸化してしまい、膜が脆くなって耐食性が悪化し易い傾向となり、平均厚さが $5 \mu m$ を超えると、前記分散水溶液中でのフレークの分散が悪くなって沈降し易くなり、処理液が不安定になって、その結果耐食性が悪くなるおそれがある。アスペクト比が2未満だとフレークが素地に

平行に積層しにくく密着不良になるおそれがある。アスペクト比の上限はないが、あまり大きいものはコスト的に高くなり、通常50以下である。

【0021】本発明で形成される皮膜において、上記金属微粉末、特にフレーク状微粉末の含有量は70wt%以上であり、より好ましくは75wt%以上である。70wt%未満では微粉末が少なすぎて、磁石素地を十分に被覆しきれないので耐食性が低下するおそれがある。また、Si、Mn、Zn、Mo、Cr、Pから選ばれる少なくとも一種の元素の酸化物は30wt%以下、より好ましくは25wt%以下（Oを含まず）を添加することがよい。

【0022】本発明において、上記耐食性皮膜を形成する方法は、上記金属微粉末と上記酸化物との分散水溶液に上記永久磁石を浸漬、又は該水溶液を永久磁石に塗布する方法が採用し得るが、この場合、まず磁石の表面に前処理を施すことが好ましい。前処理としては、酸処理、アルカリ処理、プラスト処理の中から選ばれ、

(1) 酸洗浄、水洗、超音波洗浄、(2) アルカリ洗浄、水洗、(3) ショットプラスト等から選ばれる少なくとも一種の処理を行えばよい。(1)で使用する洗浄液としては、硝酸、塩酸、酢酸、クエン酸、蟻酸、硫酸、フッ化水素酸、過マンガン酸、しゅう酸、ヒドロキシ酢酸、リン酸の中から選ばれる少なくとも一種以上を合計で1~20wt%含む水溶液を用い、これを常温以上80℃以下の温度にして希土類磁石を浸漬する。酸洗浄を行うことにより、表面の酸化皮膜を除去することができ、前記皮膜の密着力を向上させる効果がある。(2)で用いることができるアルカリ洗浄液は、水酸化ナトリウム、炭酸ナトリウム、オルソケイ酸ナトリウム、メタケイ酸ナトリウム、燐酸三ナトリウム、シアン化ナトリウム、キレート剤などの少なくとも一種以上を合計で5g/L以上200g/L以下含む水溶液であり、これを常温以上90℃以下の温度にして希土類磁石を浸漬すればよい。アルカリ洗浄は磁石表面に付着した油脂類の汚れを除去する効果があり、前記皮膜と磁石の間の密着力を向上させる。(3)のプラスト材としては通常のセラミックス、ガラス、プラスチック等を用いることができ、吐出圧力2~3kgf/cm²にて処理すればよい。ショットプラストは磁石表面の酸化皮膜を乾式で除去でき、やはり密着性を上げる効果がある。

【0023】前処理に続いて、金属微粉末と上記酸化物の分散水溶液に永久磁石を浸漬、又は該水溶液を永久磁石に塗布する。浸漬又は塗布後、加熱処理を行うが、温度は300℃以上350℃未満にて30分以上維持することが望ましい。300℃未満では成膜が不十分で密着力も耐食性も悪くなるおそれがある。また、350℃以上にすると、下地の磁石がダメージを受け、磁気特性劣化の原因になり得る。

【0024】本発明における皮膜の形成にあたっては、

繰り返して重ね塗りと加熱処理を行ってもよい。本発明における皮膜は、金属微粉末、特にフレーク状微粉末が不定形酸化物により結合された構造となる。これが高い耐食性を示す理由は定かではないが、微粉末がフレーク状である場合、これが素地に概ね平行にそり、よく磁石を被覆し、遮蔽効果を持つものと考えられる。また、フレーク状微粉末として永久磁石より卑な電位を持つ金属あるいは合金を用いたときは、これらが先に酸化され、下地の磁石の酸化を抑制する効果があると考えられる。また、この皮膜は無機物であるため、有機皮膜に比べて耐熱性が高いという特徴も有する。

【0025】このように得られた本発明の皮膜の平均厚さは1~40μmの範囲にあることが望ましい。1μm未満では耐食性が不足する場合があります。40μmを超えると、密着力低下や層間剥離を起こし易くなる場合が生じる。更に、皮膜を厚くすると、外観形状が同一であっても、使用できるR-Fe-B系永久磁石の体積が小さくなるため、磁石使用上も好ましくない。

【0026】

【実施例】以下、実施例を示し、本発明を具体的に説明するが、本発明は下記の実施例に制限されるものではない。

【0027】まず、下記方法により希土類永久磁石を製造した。Ar雰囲気の高周波溶解により、重量比で28Nd-69.8Fe-1Co-1B-0.2Alなる組成の鋳塊を作製し、Ar雰囲気下で1,070℃にて20時間溶体化処理した。これを合金1とする。次に、同じく重量比で47Nd-13Dy-18.3Fe-20Co-0.5B-1Cu-0.2Alなる組成の鋳塊をAr雰囲気の高周波溶解にて作製した。これを合金2とする。合金1と合金2のインゴットをそれぞれ別に窒素雰囲気下にてジョウクラッシャーで粗粉碎し、続いて合金1の粗粉93wt%に合金2の粗粉7wt%を秤量して、窒素置換したVブレンダーにて30分混合した。この混合粗粉を、更に窒素ガス下にてジェットミルで微粉碎し、平均粒径が3μmの微粉末を得た。この微粉末を、15kOe磁界が印加された金型内に充填し、1.0t/cm²の圧力でプレス成形した。この成形体はAr雰囲気下にて1,070℃で2時間焼結し、更に530℃で1時間時効処理を施して永久磁石とした。得られた永久磁石から径21mm×厚み10mm寸法の磁石片を切り出し、バレル研磨処理を行った後、超音波水洗を行い、これを磁石試験片とした。

【0028】この磁石の磁気特性をBHトレーサーで測定したところ、残留磁束密度Brが14.4T、保磁力iHcが1,110kA/m、最大エネルギー積が398kJ/m³であった。この磁石におけるDyの元素分布をEPMAにて調べたところ、主相の粒界付近にDyの分布が多く存在し、主相の中央にはDyの分布が少なかった。

【0029】この磁石に含まれる各種不純物元素、具体的にはC、N、O、H、P、S等の重量を、不活性ガス融解赤外吸収法、不活性ガス融解熱伝導度測定法、燃焼赤外吸収法等を用いて測定したところ、その総和は0.5wt%であった。焼結体密度は7.55g/ccであった。JIS-R-1601に準じた3点曲げ法にて抗折力を測定したところ、240MPaであった。ビッカース硬度計を用いて9.807Nの荷重にてビッカース硬さを測定したところ、600であった。

【0030】次に、皮膜形成のための処理液として、フレーク状アルミニウム粉末2wt%、フレーク状亜鉛粉末20wt%（共に平均長径3μm、平均厚さ0.2μm）、無水クロム酸4wt%が含まれた分散水溶液を準備した。前記磁石試験片表面に表1に示した前処理を行い、この分散水溶液に前記試験片を浸漬した後、10μmの膜厚になるように回転数を調整したスピコートで余滴を除去し、熱風乾燥炉で330℃にて30分加熱して前記皮膜を形成した。前処理の詳細は次の通りである。

酸洗浄

組成：硝酸10%（v/v）、硫酸5%（v/v）
50℃にて30分間浸漬

アルカリ洗浄

組成：水酸化ナトリウム10g/L、メタケイ酸ナトリウム3g/L、磷酸三ナトリウム10g/L、炭酸ナト

リウム8g/L、界面活性剤2g/L
40℃にて2分間浸漬

ショットブラスト

#220の酸化アルミニウムを用い、吐出圧力2kgf/cm²にて処理

【0031】次いで、得られた皮膜に対して下記方法で基盤目密着性試験を行った。

基盤目密着性試験

(1) JIS-K-5400基盤目試験に準ずる。カッターナイフで皮膜に1mmのマス100個ができるように基盤目状の切り傷を入れた後、セロファンテープを強く押しつけ、45度の角度に強く引いて剥がし、残った基盤目の数で密着性を評価する。

(2) 皮膜を形成した磁石に120℃、2気圧、200時間のプレッシャークッカー試験を施し、この試験後磁石に対して基盤目密着性試験を行った。試験内容はJIS-K-5400基盤目試験に準じ、カッターナイフで皮膜に1mmのマス100個ができるように基盤目状の切り傷を入れた後、セロファンテープを強く押しつけ、45度の角度に強く引いて剥がし、残った基盤目の数で密着性を評価した。前処理をしなかった比較例1と併せて表1に結果を示す。前処理を行うことにより、更に密着力が向上していることがわかる。

【0032】

【表1】

	前処理	(1)基盤目密着性試験	(2)プレッシャークッカー試験後 基盤目密着性試験
実施例1	酸洗浄+水洗+超音波洗浄	100/100	100/100
実施例2	アルカリ洗浄+水洗	100/100	100/100
実施例3	ショットブラスト	100/100	100/100
比較例1	なし	100/100	80/100

【0033】

【発明の効果】本発明によれば、高性能希土類永久磁石の表面に、好ましくは前処理を施した後、Al、Mg、Ca、Zn、Si、Mn及びこれらの合金の中から選ばれる少なくとも一種の金属の微粉末と、Si、Mn、Z

n、Mo、Cr、Pから選ばれる少なくとも一種以上の元素の酸化物を複合して形成される皮膜を密着性よく付与することにより、耐食性高性能希土類永久磁石を安価に提供することができ、産業上その利用価値は極めて高い。

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